FORM PTO-1390 (REV. 9-2001) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: Mo-4981US/MD-98-72-LS

U.S. APPLICATION NO. (If known, see 37 CFR 1.5): 10/031503 To Be Assigned

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/US00/19961	21 July 2000 (21.07.00)	23 July 1999 (23.07.99)

TITLE OF INVENTION: IN-SITU PREPARATION OF POLYASPARTIC ESTER MIXTURE

APPLICANT(S) FOR DO/EO/US: ROESLER, Richard R.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [X] The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is attached hereto (required only if not communicated by the International Bureau).
   b. [ ] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [ ] An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. [ ] is attached hereto.
   b. [ ] has been previously submitted under 35 U.S.C. 154(d)(4).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [ ] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16. [ ] A change of power of attorney and/or address letter.
17. [ ] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. [ ] A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. [ ] A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. [X] Other items or information:

Form PTO 1449 w/references

U.S. APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	531 Rec'd PCT/PTO 15 JAN 2002	ATTORNEY'S DOCKET NUMBER
To Be Assigned 10/031512	PCT/US 00/19961		Mo-4981US/MD-98-72-LS

21. [X] The following fees are submitted:	CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 0.00	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	18 - 20 =	0	x **$18.00**	$ 0.00	
Independent claims	2 - 3 =	0	x **$84.00**	$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$280.00**	$ 0.00	
TOTAL OF ABOVE CALCULATIONS =				$ 890.00	
[ ] Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.			+	$ 0.00	
SUBTOTAL =				$ 890.00	
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$ 0.00	
TOTAL NATIONAL FEE =				$ 890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 40.00	
TOTAL FEES ENCLOSED =				$ 930.00	
				Amount to be refunded:	$
				charged:	$

a. [ ] A check in the amount of $ _____ to cover the above fees is enclosed.

b. [X] Please charge my Deposit Account No. 13-3848 in the amount of $ 930.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848 . A duplicate copy of this sheet is enclosed.

d. [ ] Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

00157
PATENT TRADEMARK OFFICE

Thomas W. Roy
SIGNATURE

Thomas W. Roy
NAME

29,582
REGISTRATION NUMBER

Mo-4981
MD-98-72-LS

IN-SITU PREPARATION OF POLYASPARTIC ESTER MIXTURE

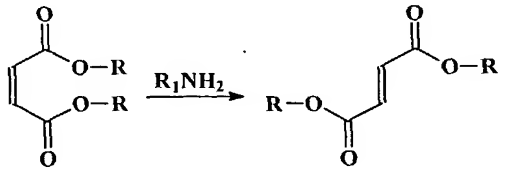
FIELD OF THE INVENTION

The invention relates to a method for making polyaspartic esters.

BACKGROUND OF THE INVENTION

Two-component coating compositions having a polyisocyanate component and an isocyanate-reactive component (a polyhydroxyl component) are known. These compositions are suitable for the preparation of high quality coatings that may be rendered rigid, elastic, resistant to abrasion and to solvents and, above, all, resistant to weathering. Polyaspartic esters have been used as isocyanate-reactive components in such two-component compositions. A polyaspartic ester can be used individually, with a polyisocyanate, or possibly in combination with polyols or polyamines. Alternatively, polyaspartic esters can be used with blocked polyamines such as ketimines, aldimines or oxizolidines.

Methods for making polyaspartic esters are known. It is known, for instance, that during the Michael Addition Reaction of an ester of fumaric or maleic acid and the primary amine, for instance, the ester of maleic or fumaric acid isomerizes to dialkyl fumarate in the presence of amines, according to the following chemical reaction:



The dialkyl fumarate is then converted to a polyaspartic ester. Mixtures of polyaspartic esters based on cyclic and acyclic amines have proven to be valuable isocyanate-reactive components of polyurea compositions that have found utility in the formulation of high solids coatings where solvent content is very low or zero. These formulations are used in architectural and automotive refinish applications. Known methods for preparing polyaspartic ester mixtures typically involve preparing polyaspartic esters

based on acyclic and cyclic amines separately and then combining each polyaspartic ester mixture. Polyaspartic esters based on acyclic amines, which contain amines attached to primary carbons, generally react with an isocyanate faster than polyaspartic esters based on cyclic amines that have an amine group attached to a secondary ring carbon. In addition, polyaspartic esters based on acyclic amines have a lower viscosity than polyaspartic esters based on cyclic amines. It is often desirable to blend these types of amines to achieve formulations with different viscosities and with intermediate reaction speeds.

U.S. Pat. No. 5,236,741 and U.S. Pat. No. 5,623,045 each disclose a single step process for the production of polyaspartic esters. Each process reacts an ester of maleic or fumaric acid with a primary polyamine such that preferably one olefinic double bond is present for each primary amino group. The patents teach that excess starting materials is removed by distillation after the reaction. Neither patent discusses how much time it takes for the reaction of the ester of maleic or fumaric acid to complete, i.e., to obtain a yield of about 100% of the polyaspartic ester. Neither patent addresses the issue of developing a process that makes a 100% yield of a mixture of (1) a polyaspartic ester based on a cyclic amine and (2) a polyaspartic ester based on an acyclic amine in a matter of days.

Unfortunately, such methods have prevented manufacturers of polyaspartic esters from delivering shipments to customers as quickly as would be desired. I have discovered that by following the teachings of the above-described known methods and using a 1:1 stoichiometric ratio, it takes several months to obtain full, or near-full, conversion of the reaction of a cyclic amine and an ester of maleic or fumaric acid. For instance, the use of bis (4-aminocyclohexyl)methane requires the polyaspartic ester to be stored in excess of six weeks to achieve 95% reaction and from six to twelve months to achieve complete reaction; and the use of bis (3-methyl-4-aminocyclohexyl)methane [commercially known as Laromin C-260] requires the polyaspartic ester to be stored in excess of eight weeks to achieve 95% reaction and from twelve to eighteen months to achieve 100% reaction. Removing excess ester of maleic or fumaric acid, as suggested by U.S. Pat. Nos. 5,236,741 and 5,623,045, is a time-consuming expensive procedure.

The problem of long waiting times has not been able to be resolved by making large amounts of the mixtures in advance because it is extremely difficult to predict customers' needs for the mixtures. Further, expensive storage, and inventory costs have discouraged the making and the storing of large amounts of the mixtures. As such, it is not uncommon for a customer to have to wait several months to receive an order of mixtures of polyaspartic esters.

It would be advantageous to develop an improved method for making mixtures of polyaspartic esters based on cyclic amines and polyaspartic esters based on acyclic amines that overcomes the above-named disadvantages.

SUMMARY OF THE INVENTION

The invention relates to a method for making a polyaspartic ester mixture *in-situ* comprising the sequential steps of (a) reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid, and (b) adding an acyclic amine to the mixture resulting from step (a) and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component. The invention is also directed to the in-situ mixture of polyaspartic ester esters formed during the method, prior to termination of the process, that contains the first polyaspartic ester component and the second polyaspartic ester component. The method makes it possible for customers to receive mixtures of the polyaspartic esters in a fraction of the time it has ordinarily taken. These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and appended claims.

DETAILED DESCRIPTION OF THE INVENTION

As used in this application, the term "cyclic amine" refers to an amine that has at least one primary amine group attached to a cyclic group, e.g., an amine attached to a secondary ring carbon. The term "acyclic amine" refers to an amine that does not have a primary amine group attached to a cyclic.

The invention is based on the discovery that mixtures of polyaspartic esters based on cyclic amines and polyaspartic esters based on

acyclic amines can be prepared *in-situ,* (under certain conditions) in a fraction of the time it ordinarily takes to make them. It is critical that the cyclic amine first react with an excess ester of maleic or fumaric acid. As discussed below, if the sequence of the steps varies, e.g., if the steps are reversed or if the cyclic and acyclic amines are added simultaneously, the reaction proceeds substantially slower and is outside the scope of the present invention.

The first and second ester components are selected from esters of maleic acid and fumaric acid. Esters of maleic acid and fumaric acid include suitable dialkyl maleates or dialkyl fumarates. Suitable dialkyl maleates include, diethyl maleate, dipropyl maleate, dibutyl maleate, methyl propyl maleate, ethyl propyl maleate, and the like. Suitable dialkyl fumigates include, diethyl fumurate, dipropyl fumurate, dibutyl fumurate, methyl propyl fumurate, ethyl propyl fumurate, and the like. Generally, dimethyl maleate or dimethyl fumurate is not used in an appreciable amount because it has been discovered that these esters cause the precipitation of long needle-like crystals that no longer participate in the Michael Addition Reaction and that cause the reaction to stop altogether. It is believed that cinnamate esters do not react under the same reaction conditions as esters of maleic acid or fumaric acid.

The amine component is generally selected from difunctional or trifunctional cyclic and acyclic amines that can accomplish the objects of the invention. Suitable amines can be selected from the following. Suitable acyclic difunctional amines include but are not limited to ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 2,5-dimethylhexane, 2,2,4- and/or 2,4,4-trimethyl-1,6-diaminohexane, 1,11-diaminoundecane, 1,12-diaminododecane, 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, 2,4- and/or 2,6-hexahydrotolylenediamine, 2,4'- and/or 4,4'-diaminodicyclohexylmethane, and 3,3'-dimethyl-4,4'-diamino-dicyclohexylmethane. Suitable cyclic amines include aromatic polyamines such as 2,4- and/or 2,6-diaminotoluene, and 2,4'- and/or 4,4'-diaminodi-phenyl-methane are also suitable but less preferred. Other suitable cyclic amines include Bis- (3-methyl-4aminocyclohexyl) methane, 2,4-diamino-1-methyl, cyclohexane, and 2,6-diamino-1-methyl cyclohexane.

Suitable trifunctional amines include 4-aminomethyl-1,8-diaminooctane (also known as triaminononane supplied by Monsanto Company), tris-(2-aminoethyl)amine. It is believed that tetrafunctional amines, e.g., N,N,N',N'-tetrakis-(2-aminoethyl)-1,2-ethanediamine are also suitable.

The polyisocyanate component used to react with the polyaspartic ester mixtures includes any polyisocyanate, which when used in accordance with the invention, meets the object of the invention. Suitable polyisocyanates for use as polyisocyanate component in accordance with the present invention include the known polyisocyanates of polyurethane chemistry. Examples of suitable low molecular weight polyisocyanates having a molecular weight of 168 to 300 include 1,4-diisocyanatobutane, 1,6-hexamethylene diisocyanate, 2,2,4- and/or 2,4,4-trimethyl-1,6-hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,4-diisocyanatocyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI), 2,4'- and/or 4,4'-diisocyanato-dicyclohexyl methane, 2,4- and/or 4,4'-diisocyanatodiphenyl methane and mixtures of these isomers with their higher homologues that are obtained in a known manner by the phosgenation of aniline/formaldehyde condenses, 2,4- and/or 2,6-diisocyanatotoluene and any mixtures of these compounds. Preferred cyclic isocyanates include diphenylmethane 4,4'-diisocyanate (MDI), diphenylmethane 2,4'-diisocyanate, 2,4- and/or 2,6-diisocyanatotoluene. Preferred aliphatic isocyanates include hexamethylene diisocyanate, isophorone diisocyanate, 2,4'- and/or 4,4'-diisocyanato-dicyclohexyl methane.

Additional suitable polyisocyanate components include derivatives of the above-mentioned monomeric polyisocyanates, as is conventional in coatings technology. These derivatives include polyisocyanates containing biuret groups as described, for example, in U.S. Pat. Nos. 3,124,605 and 3,201,372 and DE-OS 1,101,394, incorporated herein by reference in their entirety; polyisocyanates containing isocyanurate groups as described in U.S. Pat. No. 3,001,973, DE-PS 1,022,789, 1,222,067 and 1,027,394 and DE-OS 1,929,034 and 2,004,048, incorporated herein by reference in their entirety; polyisocyanates containing urethane groups as described, for instance, in DE-OS 953,012, BE-PS 752,261 and U.S. Pat. Nos. 3,394,164 and 3,644,457; polyisocyanates containing carbodiimide

groups as described in DE-PS 1,092,007, U.S. Pat. No. 3,152,162 and DE-OS 2,504,400, 2,537,685 and 2,552,350, incorporated herein by reference in their entirety; and polyisocyanates containing allophanate groups as described, for example, in GB-PS 994,890, BE-PS 761,626 and NL-OS 7,102,524. Suitable polyisocyanates also include polyisocyanates that contain uretdione groups. In one embodiment, asymmetric trimers such as those in U.S. Pat. No. 5,717,091, incorporated herein by reference in its entirety. Isocyanate group-containing prepolymers and semi-prepolymers based on polyisocyanates can also be used as the polyisocyanate component. These prepolymers and semi-prepolymers generally have an isocyanate content ranging from about 0.5 to 30% by weight, preferably about 1 to 20% by weight, and are prepared in a known manner by the reaction of starting materials, e.g., isocyanate-reactive compounds such as polyols, at an NCO/OH equivalent ratio of about 1.05:1 to 10:1, preferably about 1.1:1 to 3:1.

The first step of the process involves reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid. The equivalent ratio of the ester of maleic or fumaric acid to the cyclic polyamine is greater than 1:1, preferably 1.2:1 to 5:1 and more preferably 1.4:1 to 3:1. Generally, the more excess ester of maleic or fumaric acid used, the faster the initial reaction proceeds. To obtain a yield that is about 100% at a ratio of ester of maleic or fumaric acid to cyclic amine of 2:1, for instance, the reaction lasts less than 24 hours. When the number ratio of ester of maleic or fumaric acid to cyclic amine of 5:1, for instance, the reaction lasts less than 8 hours. It is generally preferred to have the initial reaction to be complete in about eight hours. Actual ratios for a specific application can be determined by routine experimentation.

The second step of the process involves adding an acyclic amine to the mixture and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component. The acyclic amine is preferably used in an amount that corresponds to the excess, unreacted ester of fumaric or maleic acid. Accordingly, the equivalent ratio of acyclic amine to cyclic amine is preferably 0.2:1 to 4:1,

preferably 0.4:1 to 2:1. The reaction of the excess ester of maleic or fumaric acid and the acyclic amine generally takes less than two weeks.

The reaction conditions at which the method is carried out under are discussed below. Generally, the reaction takes place at a temperature of 0 to 100°C. The reaction may take place in the absence or in the presence of suitable solvents such as methanol, ethanol, propanol, ethyl- or butyl acetate and mixtures of these solvents. The pressure of the reaction is generally atmospheric. As such, since the reaction of the cyclic polyamine and the ester of maleic or fumaric acid lasts hours instead of months, conversions of about 100% of mixtures of the polyaspartic ester based on the cyclic amine and the polyaspartic ester based on the acyclic amine can be obtained in days instead of months. Generally, a conversion of about 100% is obtained in less than 10 to 14 days.

The polyaspartic ester mixtures can be used in applications such as coatings. The low viscosity allows the formulation of paint at high or very high solids, or even paint with no solvent. Coatings applications can use polyurea coatings based on polyaspartic esters and polyisocyanates include general factory applied coating and field applied architectural or automotive refinish coatings.

The invention will now be described in the following illustrative examples. All percentages given are by weight unless otherwise indicated.

EXAMPLE 1

A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 75.6 g (0.720 eq) bis *p*-aminocyclohexyl methane (PACM) was admitted to the flask. 348.7 g (2.024 eq) diethyl maleate was admitted to the flask via the addition funnel over a one hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The temperature was maintained at 60°C for an additional five hours. The unsaturation number was 35.7 mg maleic acid per gram of resin, which indicated 100% of the PACM had been converted to aspartate. 75.6 g (1.304 eq) 1,6-hexanediamine was added to the reaction over a forty-five minute period. The reaction was heated at 60°C for four hours when the unsaturation number was 1.05, which indicated

the reaction was 97% complete. One week later the unsaturation number was 0, which indicated the reaction was 100% complete.

To determine the extent of the reaction, the unsaturation number was determined by a thiol-iodine titrametric method. This method titrates all double bonds so that the sum of both maleic and fumaric esters is included in the resultant unsaturation number. The units of unsaturation number is given in terms of milligrams maleic acid per gram of resin. Twenty-four hours later the unsaturation number was 0.66, which indicated the reaction was 98% complete.

The thiol-iodine titrametric method involved the following steps: (1) dissolving a sample in 10 ml pyridine in 100 ml flask, (2) adding 5 drops 1% solution of phenothalein indicator in ethanol, (3) dispensing 8 ml 1 N solution of 1-dodecanethiol in ethanol, (4) titrating with 0.5 N solution of sodium hydroxide in ethanol until deep purple color is achieved. (The timer was started for exactly two minutes at first contact of NaOH/ethanol solution), (5) adding 2 ml glacial acetic acid after two minutes, (6) adding 60 ml ethanol, (7) titrating with 0.1 N iodine aqueous solution until a persistent yellow color was observed, and (8) running blank with every set of titrations, and (9) calculating the maleic acid number. A nitrogen blanket was provided for steps 2 through 4.

Calculations were made in accordance to the following formula:

$$\text{maleic acid number (mg per g resin)} = \frac{(\text{blank volume} - \text{sample volume})\ 1.161}{\text{sample weight}}$$

COMPARATIVE EXAMPLE A

This example demonstrates the difference between Sequential of Example 1 and the reverse order of sequential mixing PACM and HDA). The procedure of Example 1 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 50.0 g (0.862 eq) 1,6-hexanediamine (HDA) was admitted to the flask. 230.1 g (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a one and one half hour period. The temperature of

the reaction mixture rose to 60°C as a result of a reaction exotherm. The temperature was maintained at 60°C for an additional four and one half hours. The unsaturation number was 20.0 mg maleic acid per gram of resin, which indicated 99.8 % of the HDA had been converted to aspartate.

50.0 g (.862 eq) bis *p*-aminocyclohexyl methane (PACM) was added to the reaction over a thirty minute period. The reaction was heated at 45°C for four and one half hours when the unsaturation number was 11.44, which indicated the reaction with PACM was 42 % complete. At the end of one week the unsaturation number was 5.05, which indicated the reaction with PACM was only 75 %complete. At the end of one month the unsaturation number was 1.95, which indicated the reaction was only 90% complete.

COMPARATIVE EXAMPLE B

This example demonstrates the difference between sequential process Example 1 and concurrent mixing of PACM and HDA. The procedure of Example 1 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 50.0 g (0.476 eq) PACM and 50.0 g (0.862 eq) 1,6-hexanediamine was admitted to the flask at 40°C and mixed for five minutes. 230.1 (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a two hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The reaction was held at 60°C for an additional four hours. The unsaturation number was 15.82 mg maleic acid per gram of resin, which indicated 84.0 % of the maleate had been converted to aspartate. If it is assumed that 90 % of the hexanediamine had been converted, this means that only 23 % of the PACM had been converted. After one month the unsaturation number was 1.83, which indicated 94 % of the maleate had been converted to aspartate. If it is assumed that 100 % of the hexanediamine had been converted, this means that only 89 % of the PACM had been converted after one month.

EXAMPLE 2

The procedure of Example 1 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and

nitrogen inlet. 50.0 g (0.476 eq) bis *p*-aminocyclohexyl methane (PACM) was admitted to the flask. 230.1 g (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a one and one half hour period. The temperature of the reaction mixture rose to 40°C as a result of a reaction exotherm. The temperature was maintained at 40°C for an additional four and one half hours. The unsaturation number was 36.0 mg maleic acid per gram of resin, which indicated 99.5 % of the PACM had been converted to aspartate.

50.0 g (.862 eq) 2-methyl-1,5-pentane diamine (available from DuPont as Dytek A) was added to the reaction over a forty-five minute period. The reaction was heated at 45°C for four and one half hours when the unsaturation number was 4.87, which indicated the reaction was 87 % complete. At the end of one week the unsaturation number was zero, which indicated the reaction was complete.

COMPARATIVE EXAMPLE C

The procedure of Example 2 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 150.0 g (1.43 eq) PACM and 150.0 g 2-methyl-pentane-diamine (Dytek A, available from Dupont) were admitted to the flask and mixed for five minutes. 689.7 g (4.01 eq) diethyl maleate was admitted to the flask via the addition funnel over a one hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The reaction was held at 60°C for an additional five and one half hours. The unsaturation number was 4.35 mg maleic acid per gram of resin, which indicated 90.7% of the maleate had been converted to aspartate. If it is assumed that 95% of the 2-methylpentane-diamine had been converted, this means that only 83% of the PACM had been converted.

After 11 days, the unsaturation number was 1.52, which indicated 96.8% of the maleate had been converted to aspartate. If it is assumed that 100% of the 2-methylpentane-diamine had been converted, this means that only 90.1% of the PACM had been converted after 11 days. After 18 days, the unsaturation number was 0.43, which indicated 99.1% of the maleate had been converted to aspartate. If it is assumed that 100% of the 2-methylpentane-diamine had been converted, this means that 97.4% of the PACM had been converted after 18 days.

The conversion of PACM to aspartate occurred at about the same rate as if the Dytek were not present.

COMPARATIVE EXAMPLE D

This example demonstrates the difference between the sequential process of Example 2 and the reverse order of sequential mixing PACM and Dytek A. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 50.0 g (0.862 eq) 2-methyl-1,5-pentane diamine (available from DuPont as Dytek A) was admitted to the flask. 230.1 g (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a one and one half hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The temperature was maintained at 60°C for an additional four and one half hours. The unsaturation number was 19.6 mg maleic acid per gram of resin, which indicated 100 % of the HDA had been converted to aspartate. 50.0 g (.862 eq) bis *p*-aminocyclohexyl methane (PACM) was added to the reaction over a thirty minute period. The reaction was heated at 45°C for four and one half hours when the unsaturation number was 12.26, which indicated the reaction with PACM was 37 % complete. At the end of one week the unsaturation number was 4.17, which indicated the reaction with PACM was only 79 %complete. At the end of one month the unsaturation number was 1.92, which indicated the reaction was only 90% complete.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. A method for making a polyaspartic ester mixture in-situ comprising the sequential steps of:

(a) reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing a first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid, and

(b) adding an acyclic amine to the mixture resulting from step (a) in an amount sufficient to react the acyclic amine with the excess ester of fumaric or maleic acid and to form a second polyaspartic ester component.

2. The method of Claim 1, wherein the cyclic amine comprises a component selected from the group consisting of 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, hexahydro-2,4- diaminotoluene, hexahydro-2,6-diaminotoluene, alkyl substituted cyclohexanediamines 2,4'- and/or 4,4'-diamino-dicyclo-hexylmethane, 3,3'-dimethyl-4,4'-diaminodicyclohexyl-methane, isomers of diaminodicyclohexylmethane having a methyl group as a substituent, and 3,4-aminomethyl-1-methylcyclohexylamine.

3. The method of Claim 1, wherein the acyclic amine comprises a component selected from the group consisting of ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 2-methyl-1,5-diaminopentane, 2,5-diamino-2,5-dimethylhexane, 2,2,4-trimethyl-1,6-diaminohexane, 2,4,4-trimethyl-1,6-diaminohexane, 1,11-diaminoundecane, and 1,1,2-diaminododecane.

4. The method of Claim 1, wherein the ester of fumaric or maleic acid comprises an ester selected from the group consisting of diethyl maleate, dipropyl maleate, dibutyl maleate, methyl propyl maleate, ethyl propyl maleate, diethyl fumurate, dipropyl fumurate, dibutyl fumurate, methyl propyl fumurate, and ethyl propyl fumurate.

5. The method of Claim 1, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is at least 2:1.

6. The method of Claim 1, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is from about 20:1 to about 2:1.

7. The method of Claim 1, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 20 days.

8. The method of Claim 1, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 8 days.

9. A method for making a polyaspartic ester mixture in-situ comprising the sequential steps of:

(a) reacting a cyclic amine with an ester of fumaric or maleic acid to form a mixture containing a first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is at least 2:1 and

(b) adding an acyclic amine to the mixture resulting from step (a) and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 20 days.

10. The method of Claim 9, wherein the cyclic amine comprises a component selected from the group consisting of 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, hexahydro-2,4- diaminotoluene, hexahydro-2,6-diaminotoluene, alkyl substituted cyclohexanediamines 2,4'- and/or 4,4'-diamino-dicyclo-hexylmethane, 3,3'-dimethyl-4,4'-diaminodicyclohexyl-methane, isomers of diaminodicyclohexylmethane having a methyl group as a substituent, and 3,4-aminomethyl-1-methylcyclohexylamine.

11. The method of Claim 9, wherein the acyclic amine comprises a component selected from the group consisting of ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 2-methyl-1,5-diaminopentane, 2,5-diamino-2,5-dimethylhexane, 2,2,4-trimethyl-1,6-

diaminohexane, 2,4,4-trimethyl-1,6-diaminohexane, 1,11-diaminoundecane, and 1,1,2-diaminododecane.

12. The method of Claim 9, wherein the ester of fumaric or maleic acid comprises an ester selected from the group consisting of symmetrical esters, and asymmetrical esters.

13. The method of Claim 9, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is at least 2:1.

14. The method of Claim 9, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is from about 20:1 to about 2:1.

15. The method of Claim 9, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 20 days.

16. The method of Claim 9, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 8 days.

17. An in-situ mixture of polyaspartic ester esters formed during the method of Claim 9, prior to termination of the process, comprising the first polyaspartic ester component and the second polyaspartic ester component.

18. An in-situ mixture of polyaspartic ester esters formed during the method of Claim 17, prior to termination of the process, comprising the first polyaspartic ester component and the second polyaspartic ester component.

IN-SITU PREPARATION OF POLYASPARTIC ESTER MIXTURE

ABSTRACT OF THE DISCLOSURE

A method for making a polyaspartic ester mixture *in-situ* comprising the sequential steps of (a) reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid, and (b) adding an acyclic amine to the mixture resulting from step (a) and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component.

Attorney Docket No.
Mo4981/MD-98-72-LS

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that

My residence, post office and address and citizenship are as stated below next to my name,

I believe I am the original, and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

IN-SITU PREPARATION OF POLYASPARTIC ESTER MIXTURE

the specification of which (check one)

☒ is attached hereto

was filed on 23/07/99 as Application Serial No. PCT/US00/19961 and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with title 37, Code of Federal Regulations, §1.56 (a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below and foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)			Priority claimed
PCT/US00/19961	World	21/07/00	■ Yes ☐ No
(Number)	(Country)	(Day/month/year filed)	
			☐ Yes ☐ No
(Number)	(Country)	(Day/month/year filed)	
			☐ Yes ☐ No
Number)	(Country)	(Day/month/year filed)	

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

60/145,455	21 July 1999	Pending
(Application Serial No.)	(Filing Date)	(STATUS: patented/pending/abandoned)
(Application Serial No.)	(Filing Date)	(STATUS: patented/pending/abandoned)

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office Connected therewith:

(15)

JOSEPH C. GIL, Patent Office Registration Number 26,602
ARON PREIS, Patent Office Registration Number 29,426
LYNDANNE M. WHALEN, Patent Office Registration Number 29,457
THOMAS W. ROY, Patent Office Registration Number 29,582
RICHARD E.L. HENDERSON, Patent Office Registration Number 31,619
GODFRIED R. AKORLI, Patent Office Registration Number 28,779
N. DENISE BROWN, Patent Office Registration Number 36,097
NOLAND J. CHEUNG, Patent Office Registration Number 39,138
DIDERICO VAN EYL, Patent Office Registration Number 38,641
CAROLYN M. SLOANE, Patent Office Registration Number 44,339
JAMES R. FRANKS, Patent Office Registration Number 42,552
JACKIE ANN ZURCHER, Patent Office Registration Number 42,251
RAYMOND J. HARMUTH, Patent Office Registration Number 33,896
JOHN E. WROZINSKI, JR. Patent Office Registration Number 46,179
JENNIFER R. SENG, Patent Office Registration Number 48,851

all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

SEND CORRESPONDENCE TO:	DIRECT TELEPHONE CALLS TO:
Patent Department Bayer Corporation 100 Bayer Road Pittsburgh, Pennsylvania 15205-9741	Patent Department (412) 777-8349

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00

FULL NAME OF SOLE OR FIRST INVENTOR	INVENTOR'S SIGNATURE	DATE
Richard R. Roesler	Richard R Roesler	1/11/02
RESIDENCE		CITIZENSHIP
863 Hillcrest Circle, Wexford, PA 15090-7583 PA		U.S. Citizen
POST OFFICE ADDRESS		
Bayer Corporation, 100 Bayer Road, Pittsburgh, PA 15205-9741		
FULL NAME OF SECOND JOINT INVENTOR, IF ANY	INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP
POST OFFICE ADDRESS		
FULL NAME OF THIRD JOINT INVENTOR, IF ANY	INVENTOR'S SIGNATURE	DATE
POST OFFICE ADDRESS		CITIZENSHIP
POST OFFICE ADDRESS		
FULL NAME OF FOURTH JOINT INVENTOR, IF ANY	INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP
POST OFFICE ADDRESS		
FULL NAME OF FIFTH JOINT INVENTOR, IF ANY	INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP
POST OFFICE ADDRESS		

/vjt/4981declaration